華中科技大學
Huazhong University of Science & Technology

Partitioning of inorganic constituents during O_2/CO_2 combustion and CO_2 mineral sequestration

Dr. Junying ZHANG

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

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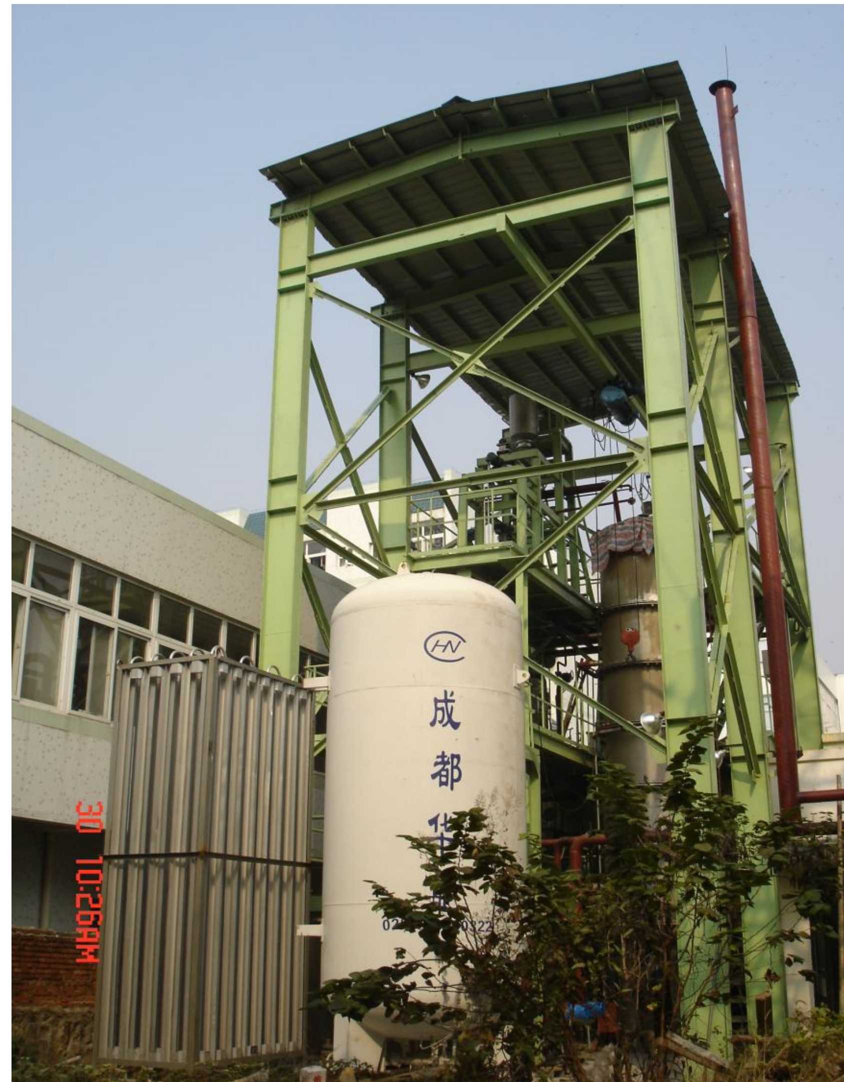
Outline

- ***Minerals thermal behavior in oxy-fuel combustion***

- ***CO_2 sequestration by mineral carbonation***

1. O_2/CO_2 combustion pilot-scale system



- Technical parameters:
  - (1) 0.3MW;
  - (2) O_2: 60NM3/h; CO_2: 240NM3/h
- Occupy area：~200M2
- Height：12.5m
- Investment：4,000,000¥

Function

- High temperature air combustion
- O_2/CO_2 flue gas recycle
- Ca-based sorbents injection desulfurization
- low NOx combustion
- Multiple dust collecting equipment
- Multi-Pollution control simultaneously

Current Research and Progress

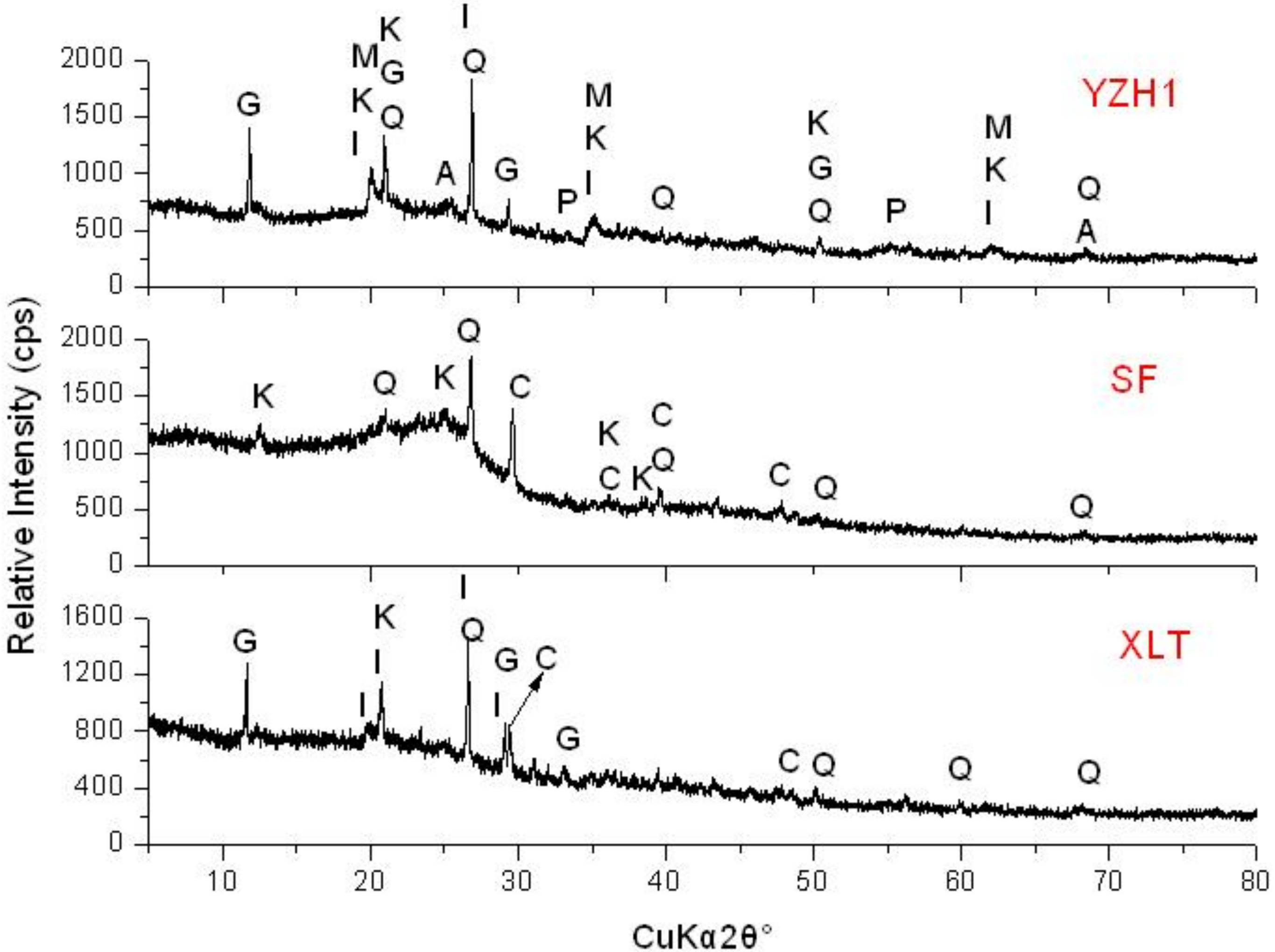
- Air combustion tests—Baseline
- O_2/CO_2 combustion tests
  - Outlet CO_2 concentration is up to 90%
  - Outlet O_2 concentration: 4%
- O_2/CO_2 combustion + FGR tests
  - flue gas Recycle 30%
  - Outlet flue gas: CO_2-90%，O_2-8%，NO_x-260ppm

2. Minerals thermal behavior in O_2/CO_2

- Three typical coal samples used in experiments: Xiaolongtan (XLT), Shenfu (SF), and Yangzonghai1 (YZH1).
- Low temperature ash (LTA) was prepared at low temperature for about 12-24 hours in a K1050X plasma asher from EMITECH.
- TG-DTA
  - Samples: coal, LTA
  - Heating rate: 20K/min, 50K/min
  - Atmosphere: O_2/N_2=1:4, O_2/CO_2=1:4
  - Temperature: 1450℃
- Mineral composition:
  - XRD
  - Semi-quantity calculation

NETZSCH STA 409 thermogravimetric analyzer

Minerals in coals



- G:gypsum
- K:kaolinite
- I:illite
- Q:quartz
- A:anatase
- P:pyrite
- C:calcite
- M:Montmorillonite

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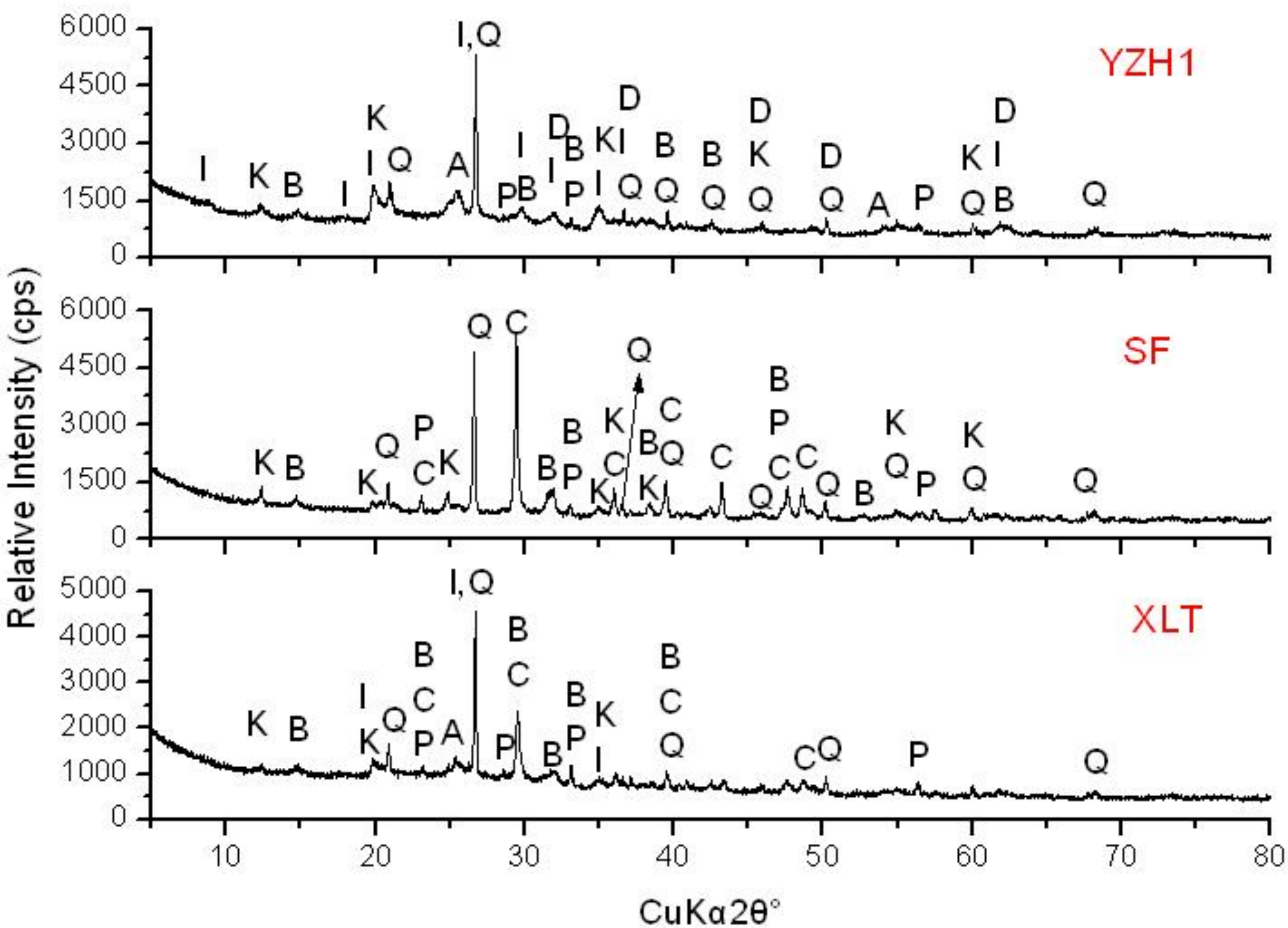
Minerals in LTAs



- D:dolomite
- K:kaolinite
- I:illite
- Q:quartz
- A:anatase
- P:pyrite
- C:calcite
- B:bassanite

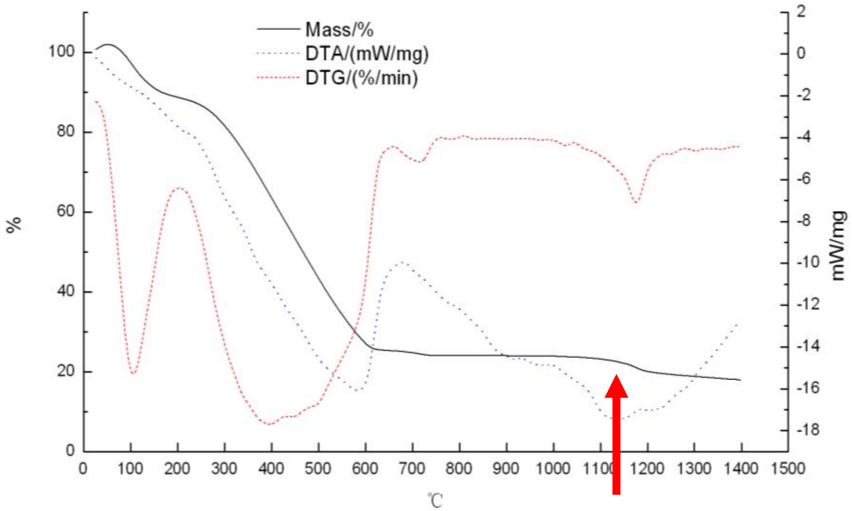
Semi-quantity of mineral composition

Mineral composition of three typical high calcium coals and their LTAs (wt.%)

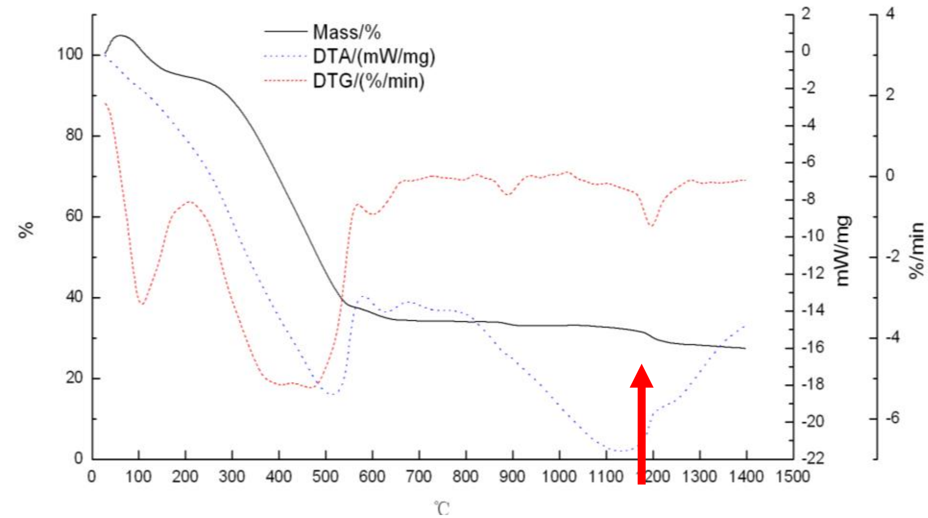
	Xiaolongtan		Shenfu		Yangzonghai1	
	Coal	LTA	Coal	LTA	Coal	LTA
Organic	82.1		89.8		59.0	
Minerals	17.9		10.2		41.0	
Kaolinite	2.5	8.8	4.5	12.7	6.2	16.9
Montmorillonite					3.4	
Illite	5.2	21.0			7.6	25.0
Quartz	4.3	19.1	3.1	30.6	6.7	18.6
Calcite	1.4	15.4	2.6	40.6		
Gypsum	4.4				9.1	
Bassanite		26.3		10.1		15.9
Dolomite						10.6
Pyrite		2.8		5.2	2.2	5.3
Anatase		4.0			5.9	7.7

Thermal behavior of coals

O2/N2



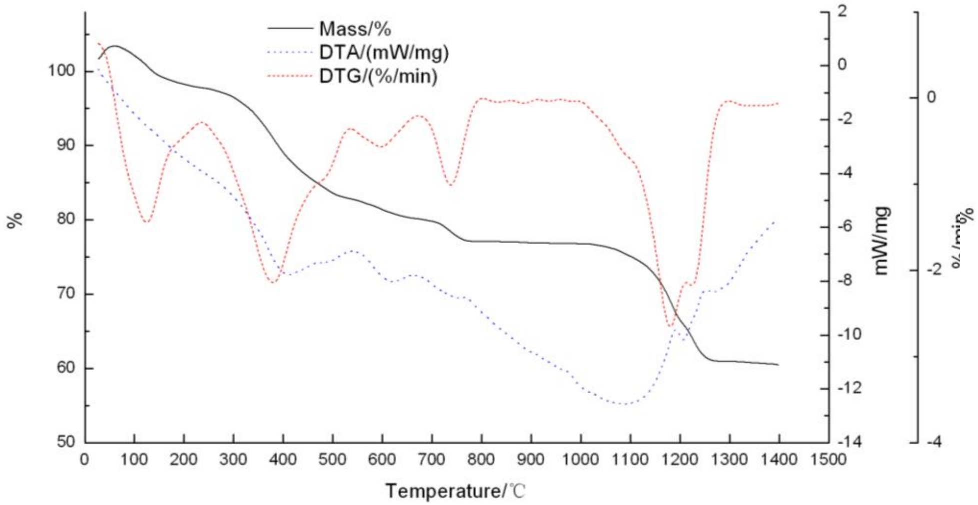
O2/CO2



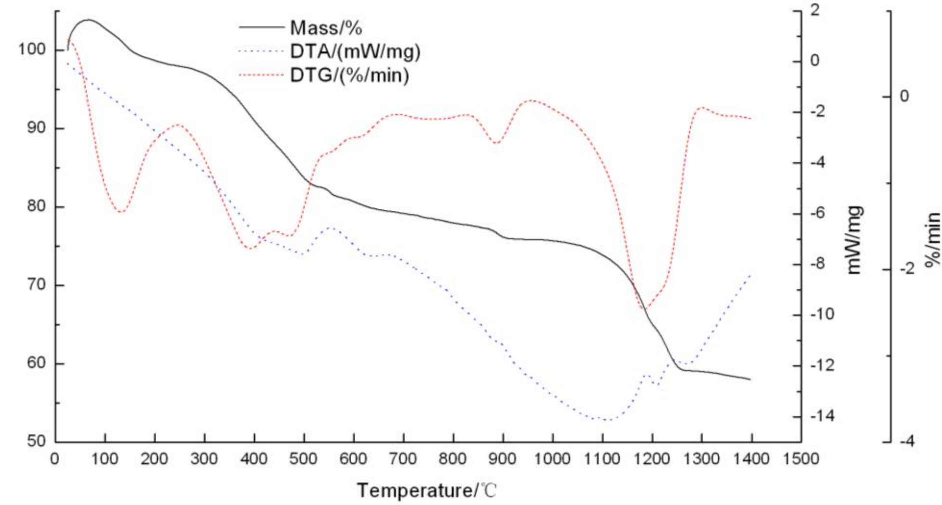
- The elimination of physically adsorbed water
- Releasing of volatile matter and combustion of the carbonaceous materials
- Burnout stage, transformation of minerals
- Vaporization of some volatile mineral elements

Thermal behavior of LTAs

O2/N2



O2/CO2



- Mineral in LTA mainly include: clay minerals, quartz, carbonates, sulfides and sulfates, etc.
- TGA curves of LTA are similar with the coal
- Loss of adsorbed moisture and water of crystallization
- Mineral melt and volatile mineral elements vaporization

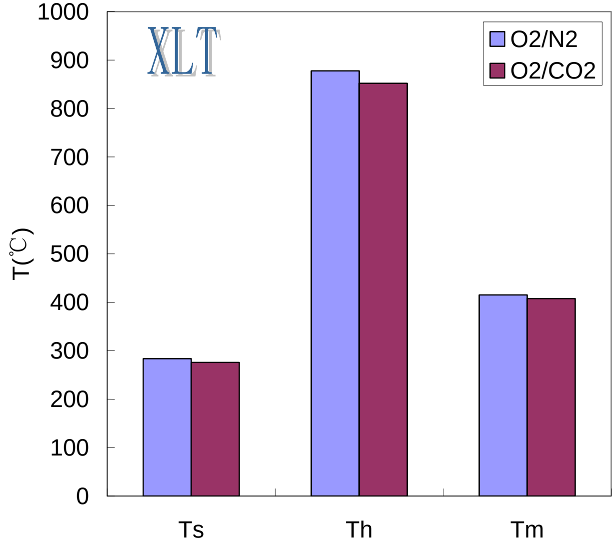
Characteristics temperature

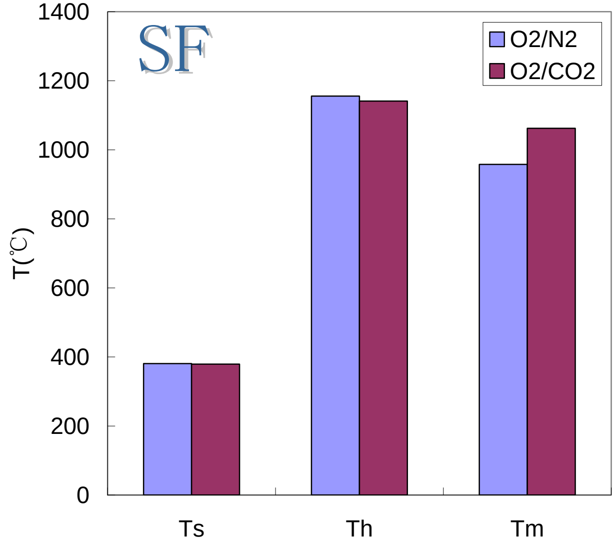
Characteristic temperature of coal in different conditions

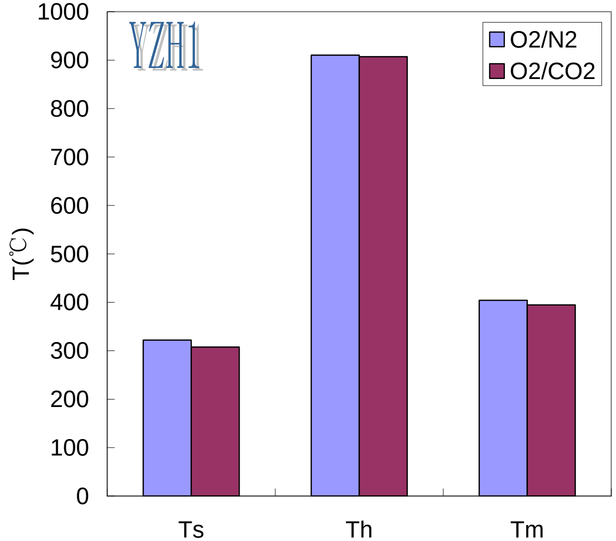
Sample	Atmosphere	50℃/min			20℃/min		
		T_s	T_h	T_m	T_s	T_h	T_m
YZH1-Coal	O_2/N_2	283.5	877.7	415.1	305.2	585.9	502.2
	O_2/CO_2	275.8	852	407.5	278.5	536.4	497
SF-Coal	O_2/N_2	380.6	1155.6	957.7	367.7	869.3	494.5
	O_2/CO_2	379.1	1141.2	1062.2	365.8	595.3	489.5
XLT-Coal	O_2/N_2	321.9	910.3	404.1	283	606.6	487.1
	O_2/CO_2	307.6	907	394.6	277.8	544.4	470.1

- Firing temperature (T_s), the peak temperature at maximum weight loss rate(T_m), burnout temperature (T_h)

Atmosphere influence







- Compared with air atmosphere, the firing temperature (Ts), the peak temperature at maximum weight loss rate(Tm), burnout temperature (Th) are lower in O_2/CO_2 condition.

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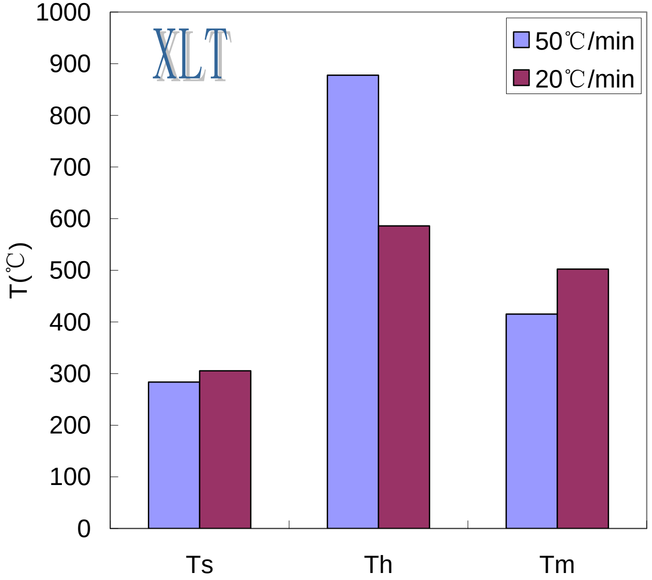
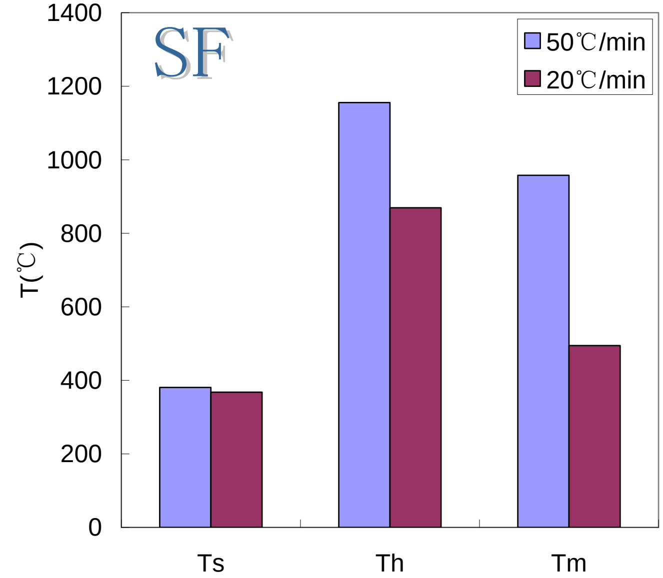
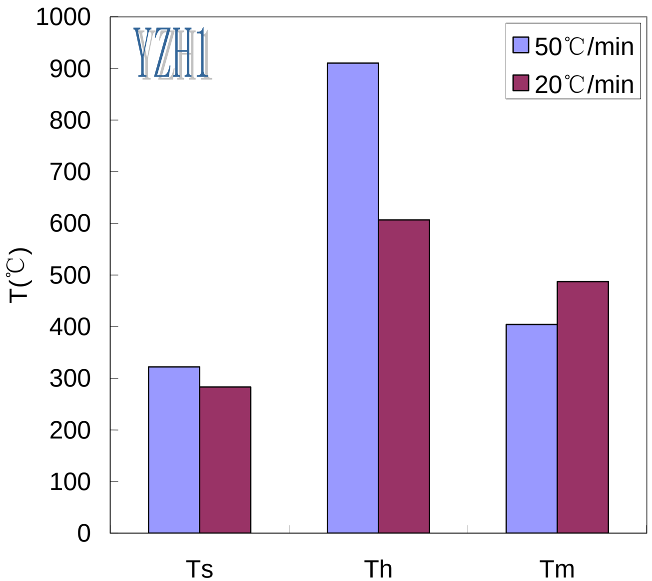
Heating rate influence







- The characteristic temperatures show less regularity in different heating rates. However, the all of the Th increased with the increasing of heating rate.

Mineral vaporization

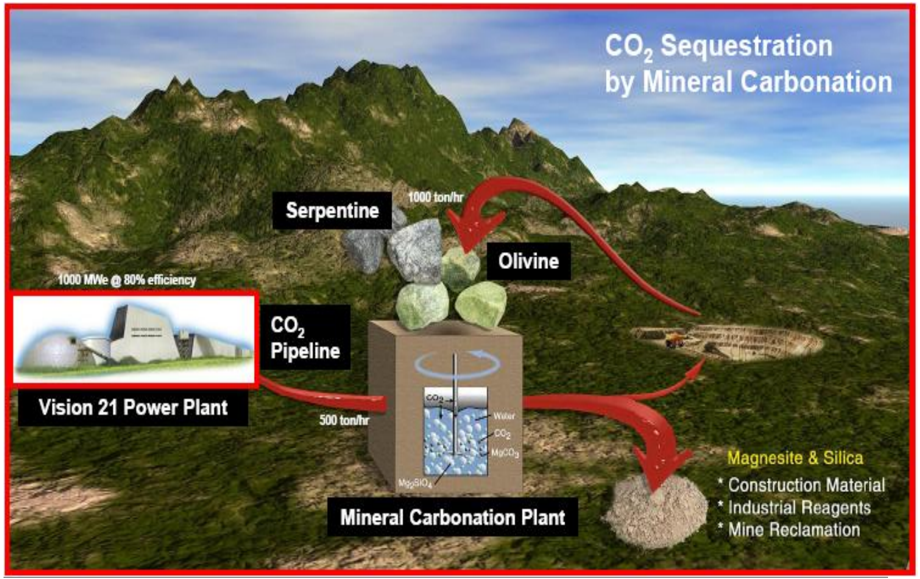
Mineral elements vaporization of YZH coal and its LTA (wt.%) (m_{LTA}/m_{coal}=0.1786)

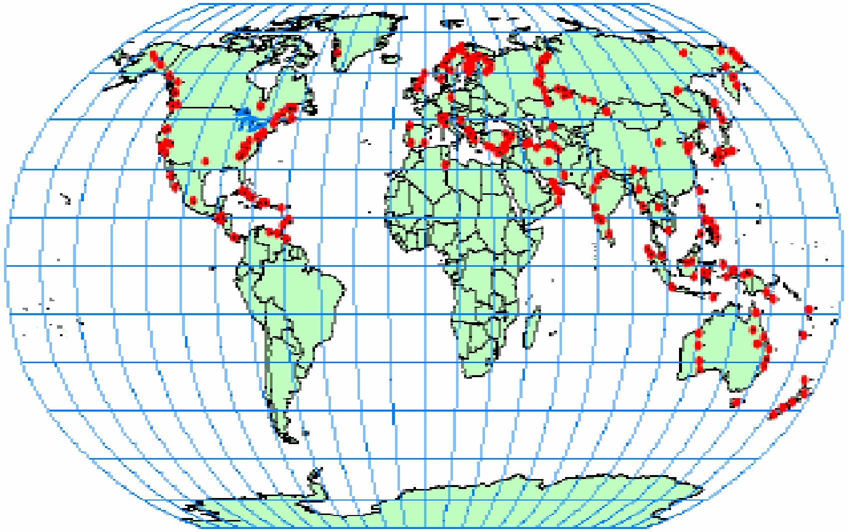
Temperature (℃)	50K/min				20K/min			
	Coal		LTA		Coal		LTA	
	O_2/N_2	O_2/CO_2	O_2/N_2	O_2/CO_2	O_2/N_2	O_2/CO_2	O_2/N_2	O_2/CO_2
1100~1150	0.11	0.30	0.43	0.32	0.17	0.23	0.39	0.17
1150~1200	0.42	0.43	0.51	0.51	0.42	0.42	0.58	0.39
1200~1250	0.30	0.20	0.27	0.26	0.24	0.08	0.21	0.11
1250~1300	0.18	0.16	0.06	0.03	0.15	0.07	0.05	0.11
1300~1350	0.13	0.05	0.08	0.02	0.13	0.07	0.03	0.08
1350~1400	0.21	0.05	0.03	0.06	0.15	0.20	0.01	0.15
Total vaporization amount	1.35	1.19	1.38	1.20	1.25	1.07	1.27	1.01

The total mineral element vaporization amount is higher in O2/N2 atmosphere than in O2/CO2 atmosphere.

- Compared with air atmosphere, the characteristics temperature (T_s, T_m, T_h) are lower in O_2/CO_2 combustion atmosphere.
- The organic matter in coal will promote the vaporization of mineral elements, especially in O_2/CO_2 mixture atmosphere. The total mineral element vaporization amount is higher in O_2/N_2 atmosphere than in O_2/CO_2 atmosphere.

3. CO_2 Mineral Carbonation





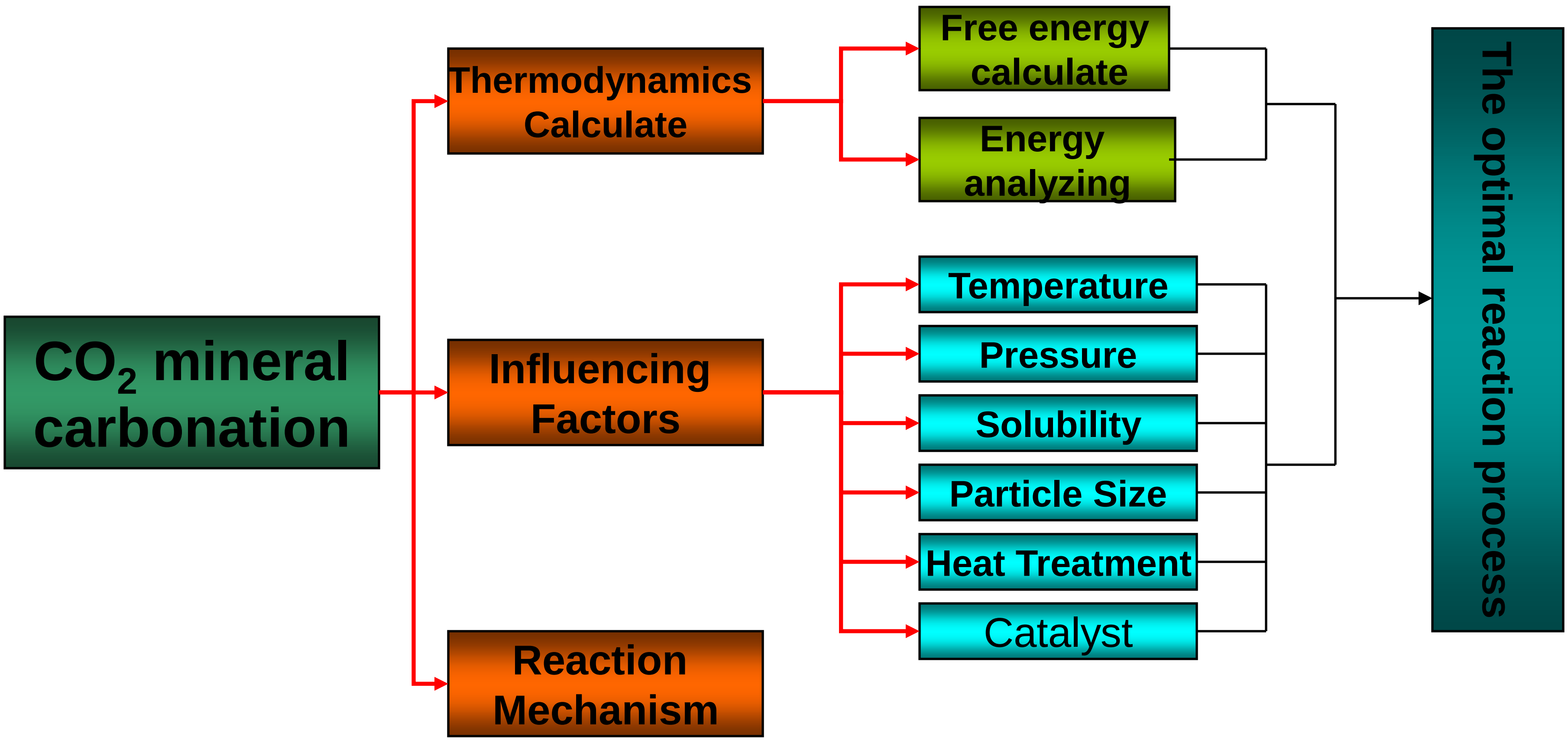
- Abundant reserves of minerals which can capture CO_2 without second pollution;
- Low energy consumption, exothermic reaction;
- Different carbon fund organizations will promote the development of CO_2 reduction emission technical

Background

- **1990, Seifritz, W. CO_2 disposal by means of silicates. *Nature* 1990,*345*, 486.**
- **1995, Klaus S, Lackner and Christopher W.H. Carbon dioxide disposal in carbonate minerals. Energy,1995,20(11):1153-1170**
- **2000, O'Connor, W. K et al. Carbon dioxide sequestration by direct mineral carbonation. *Mineral. Metall.Process.* 2002, *19* (2), 95-101.**
- **2005, W. Huijgen, et al.Mineral CO_2 Sequestration by Steel Slag Carbonation. Environ. Sci. Technol. 2005, 39, 9676-9682**

- mineral carbonation, as originally proposed by Seifritz and first studied in more detail by Lackner et al.

Technology Roadmap



Purposes of this work:

- Increase the reaction rate of mineral carbonation under middle and low pressure
- Provide some theoretical and technical supports for the effective control of CO_2 emission.

CO_2 Mineral Carbonation

- **The family of reactions:**
- **(Mg, Ca)xSiyOx+（2y+z）H_2 （z+x）CO_2 → x(Mg,Ca)CO_3 + ySiO_2 +zH_2O**

- **Serpentine:**
- **MgO38-45%(wt%)**
- **$Fe_2O_3$5-8 %(wt%)**
- **H_2O13 %(wt%)**
- **Reaction releases heat： + 64 kJ/mole**
- **One ton of serpentine can dispose of**
- **approximately one-half ton of CO_2**

- **Olivine：**
- **MgO45-50%(wt%)**
- **Fe2O3 6-10%(wt%)**
- **Reaction releases heat：+ 95 kJ/mole**
- **One ton of olivine can dispose of**
- **approximately two-thirds of a ton of CO_2**

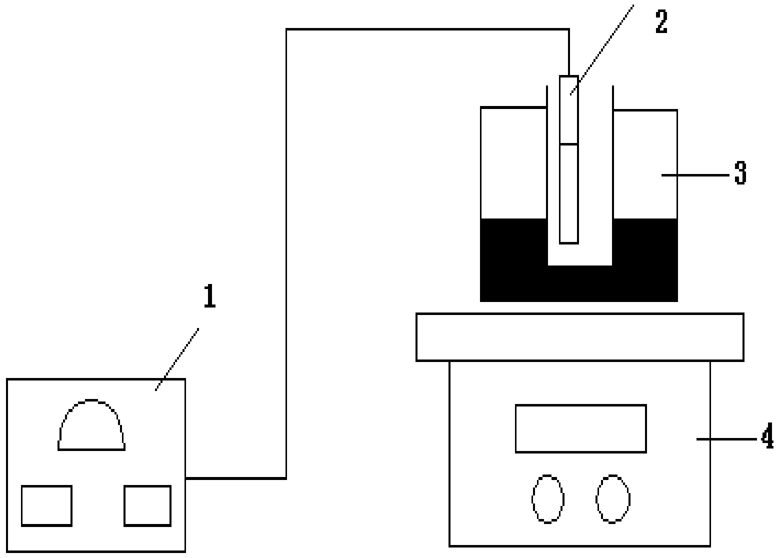
Problem: **The reaction rate of mineral carbonation under natural conditions is too slow to use in the large-scale commercial CO2 sequestration programs.**

3.1 Mineral Carbonation-dissolution of mineral

Condition

1	H_2O，　25℃，150r/min
2	H_2O，　25℃ ，0
3	H_2O，　50℃ ，150r/min
4	H_2O，　50℃ ，0
5	H_2O，　75℃ ，150r/min
6	H_2O，　100℃ ，150r/min

Experiment Platform



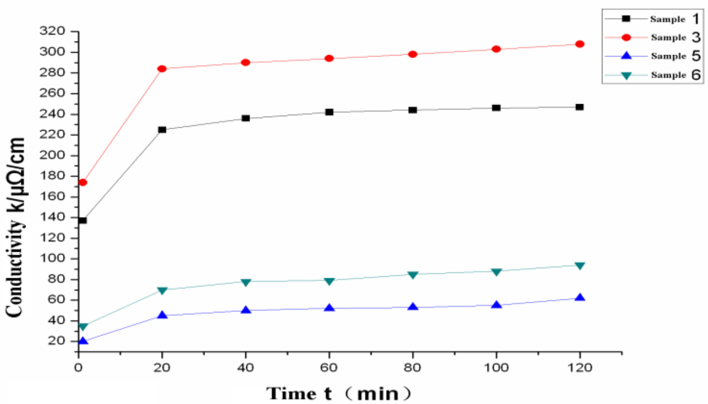
1. **Conductivity Meter；2. Conductivity Probe；3. Constant Temperature Water Bath；4. Oscillator**

Samples

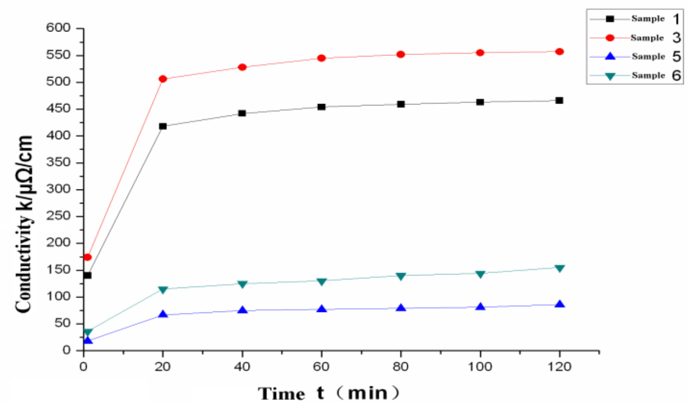
1	**Serpentine, 74μm**
2	**Serpentine, 74μm,, heat-treated in air at 650℃ for 2hours**
3	**Serpentine, 30μm**
4	**Serpentine, 30μm, heat-treated in air at 650℃ for 2hours**
5	**Olivine, 74μm**
6	**Olivine, 30μm , heat-treated in air at 650℃ for 2hours**

Effect of Particle Size on Mineral Dissolution

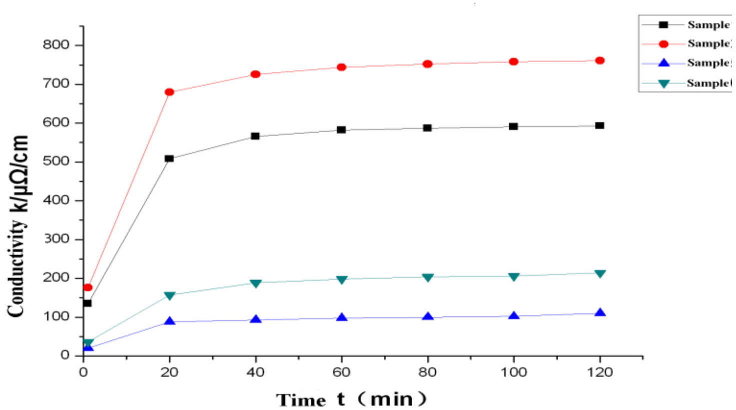
25℃



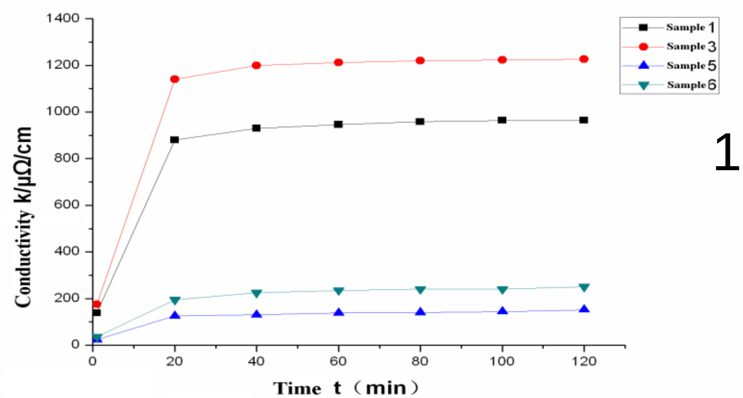
50℃



75℃



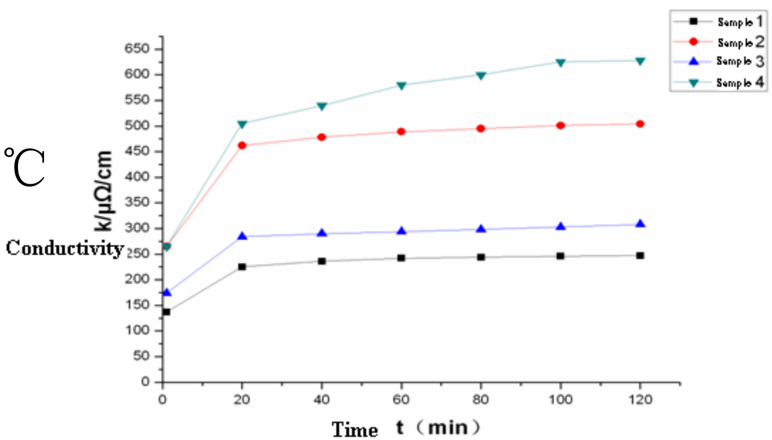
100℃



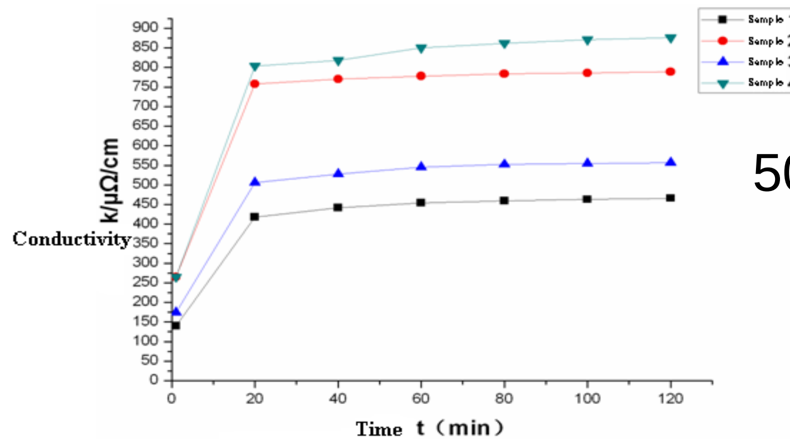
The surface area of the mineral particles increases with particle size decreases. In the crushing and screening process, the solubility of mineral increases.

Effect of Heat Treatment on Mineral Dissolution

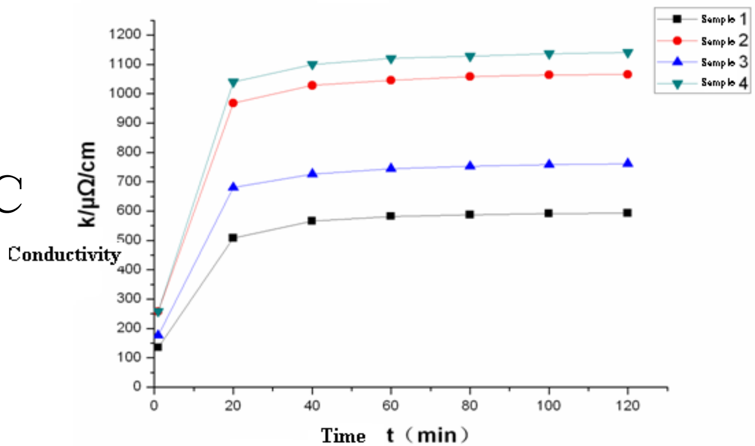
25℃



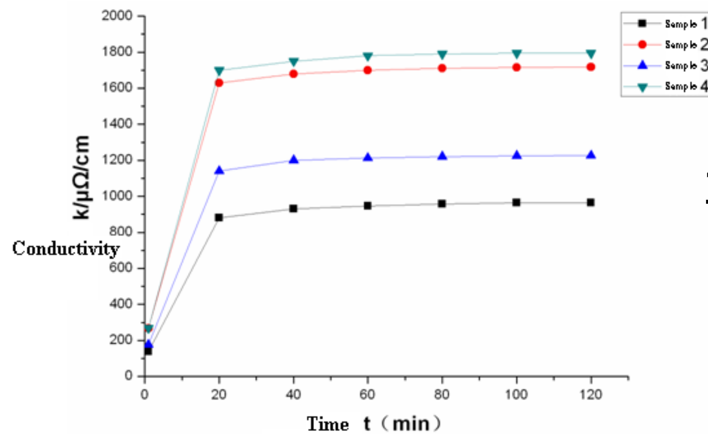
50℃



75℃

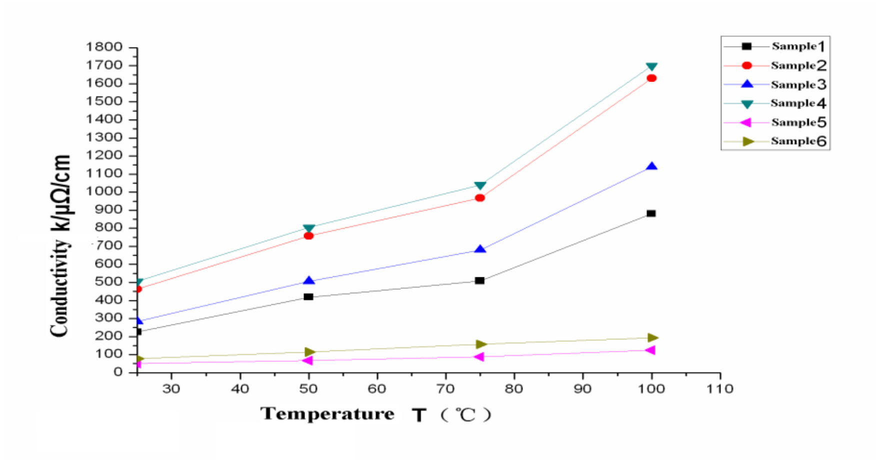


100℃

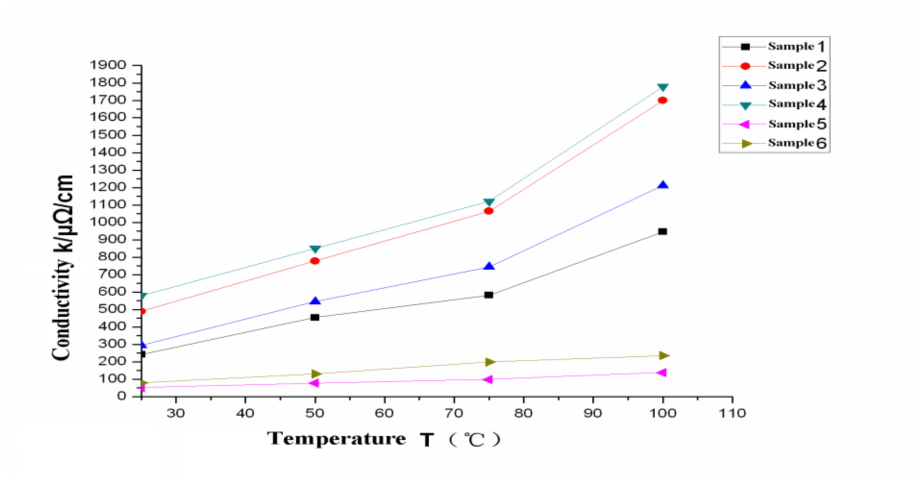


Heat treatment can reduce the water content in the mineral particles, the solubility of mineral increases.

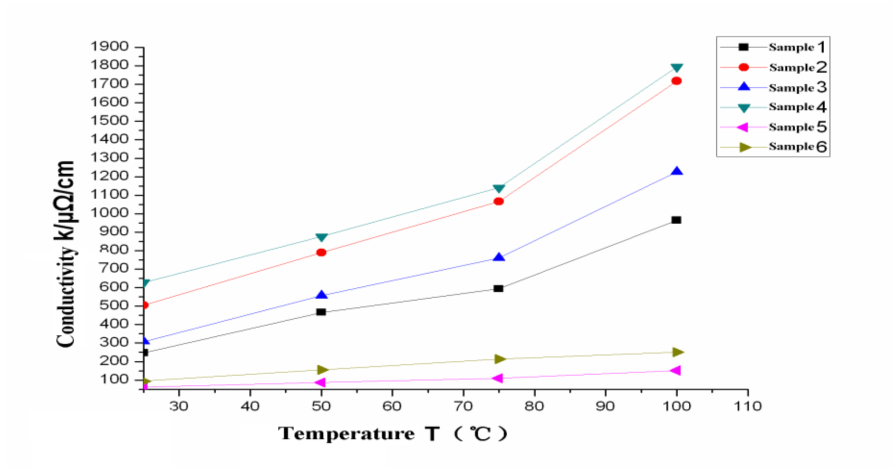
Effect of Temperature on Mineral Dissolution



20min



60min



120min

The solubility of mineral increases with the temperature increasing.

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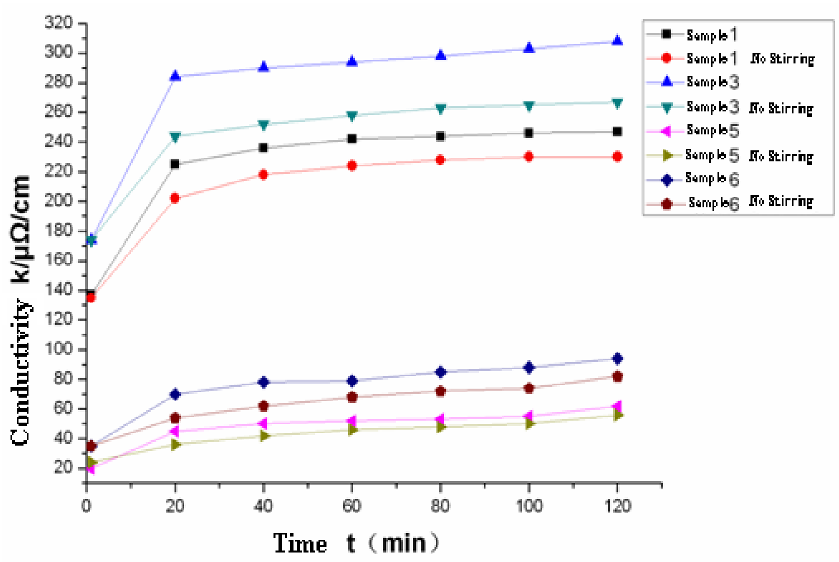
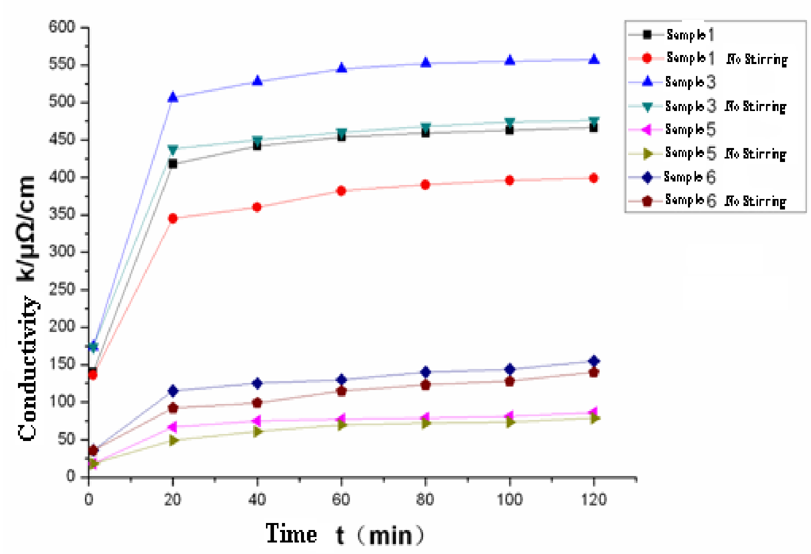
Effect of Stirring on Mineral Dissolution



25℃



50℃

Stirring can not only help the mineral particles contact with the water, but also can weaken the inhibition of attachment layers, the solubility of mineral increases.

3.2 Mineral Carbonation ——Pure CO2

The Reaction Condition of Serpentine

Example	Reaction Condition
1	P=10MPa;T=155℃; RT=60min;PS=74μm； heat-treated in air at 650℃ for 2hours
2	P=7MPa; T=155℃; RT=60min; PS=74μm； heat-treated in air at 650℃ for 2hours
3	P=10MPa;T=155℃; RT=60min; PS=37μm； heat-treated in air at 650℃ for 2hours
4	P=10MPa;T=155℃; RT=60min; PS=74μm； untreated
5	P=7MPa; T=50℃; RT=60min; PS=74μm； heat-treated in air at 650℃ for 2hours
6	P=7MPa; T=100℃; RT=60min; PS=74μm； heat-treated in air at 650℃ for 2hours
7	P=7MPa; T=150℃; RT=60min; PS=74μm； heat-treated in air at 650℃ for 2hours
8	P=7MPa; T=200℃; RT=60min; PS=74μm； heat-treated in air at 650℃ for 2hours

*RT——reaction time

PS——particle size

The Reaction Condition of Wollastonite

Numble	Reaction Condition
1	P=4MPa，T=80℃， RT=60min PS=30~74μm untreated
2	P=4MPa，T=100℃， RT=60min PS=30~74μm untreated
3	P=4MPa，T=150℃， RT=60min PS=30~74μm untreated
4	P=4MPa，T=200℃， RT=60min PS=30~74μm untreated
5	P=2MPa，T=150℃， RT=60min PS=30~74μm untreated
6	P=4MPa，T=150℃， RT=60min PS<30μm untreated
7	P=6MPa，T=150℃， RT=60min PS=30~74μm untreated
8	P=7MPa，T=150℃， RT=60min PS=30~74μm untreated

*RT——reaction time

PS——particle size

Mineralogy composition of production

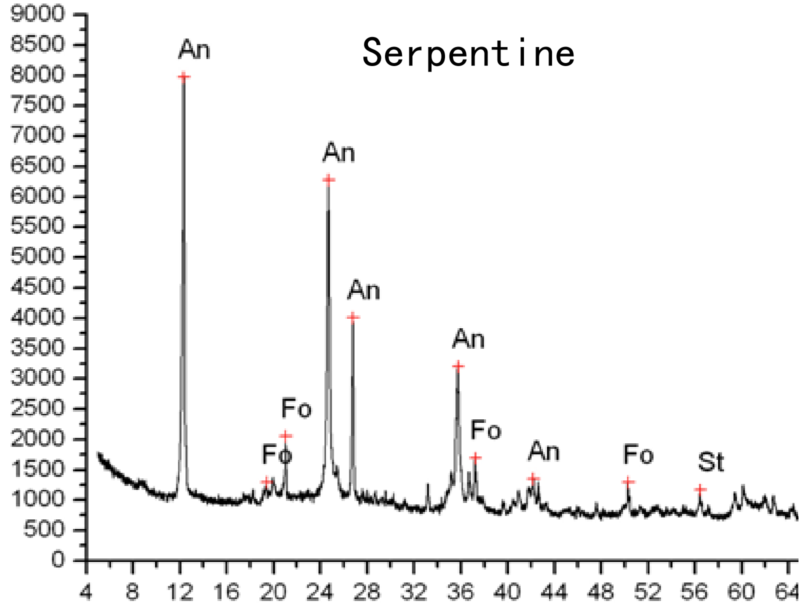


Figure a

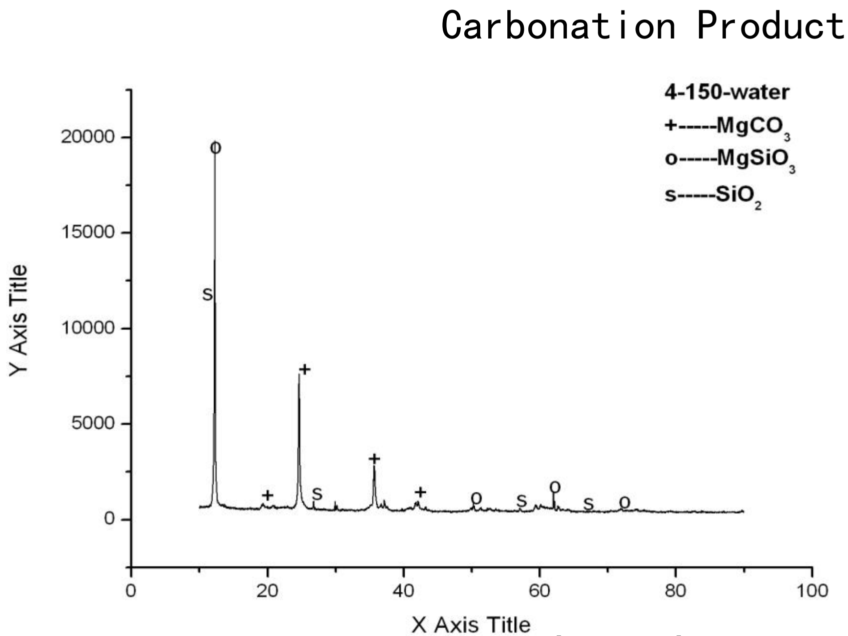


Figure b

*antigorite (An), forsterite (Fo), calcium fluoride (St), magnesite (Ms)

Figure a is the XRD analysis of Serpentine sample. Figure b is the XRD analysis of the carbonation product. The results show that magnesite is existed in the product and also the silica, which indicate that the following reaction has taken place:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$

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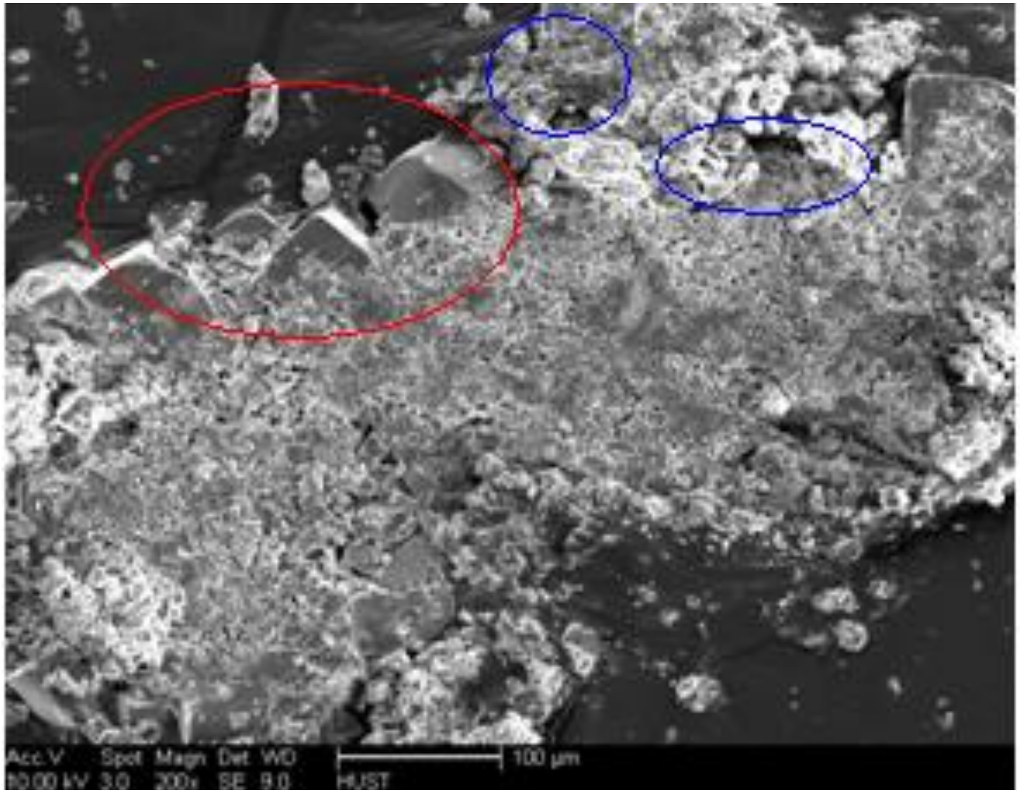
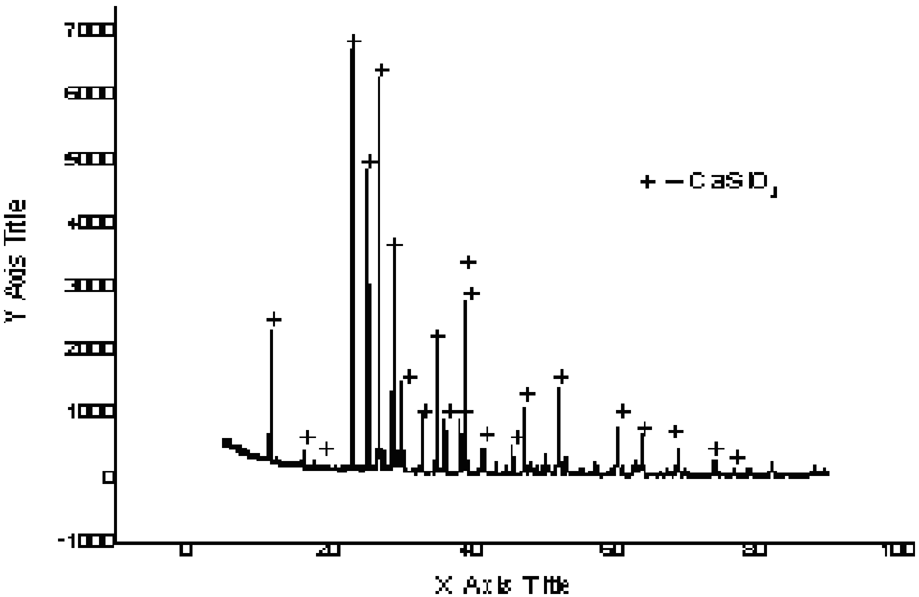
SEM of carbonation production



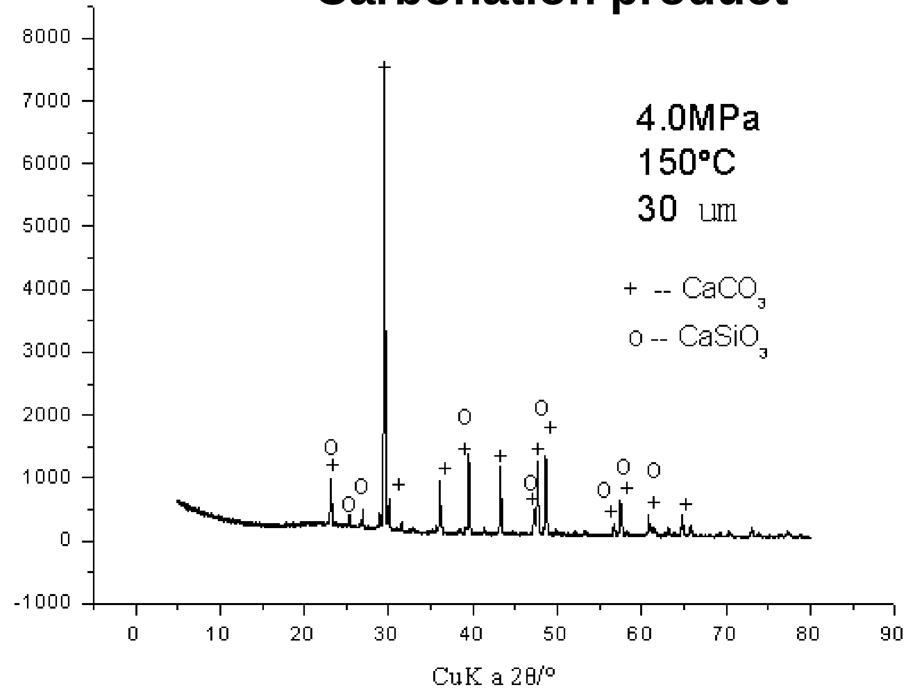
- Serpentine heat-treated reaction product. SEM analysis showing the rhombus magnesite (the red loop) and some serpentine particles (the blue loop) around it.

Product Analysis-Wollastonite

Wollastonite



Carbonation product



The left is the XRD analysis of Wollastonite sample, right is the XRD analysis of the product. The results show Calcium carbonate existed in the product. It can prove that the following reaction must have taken place:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

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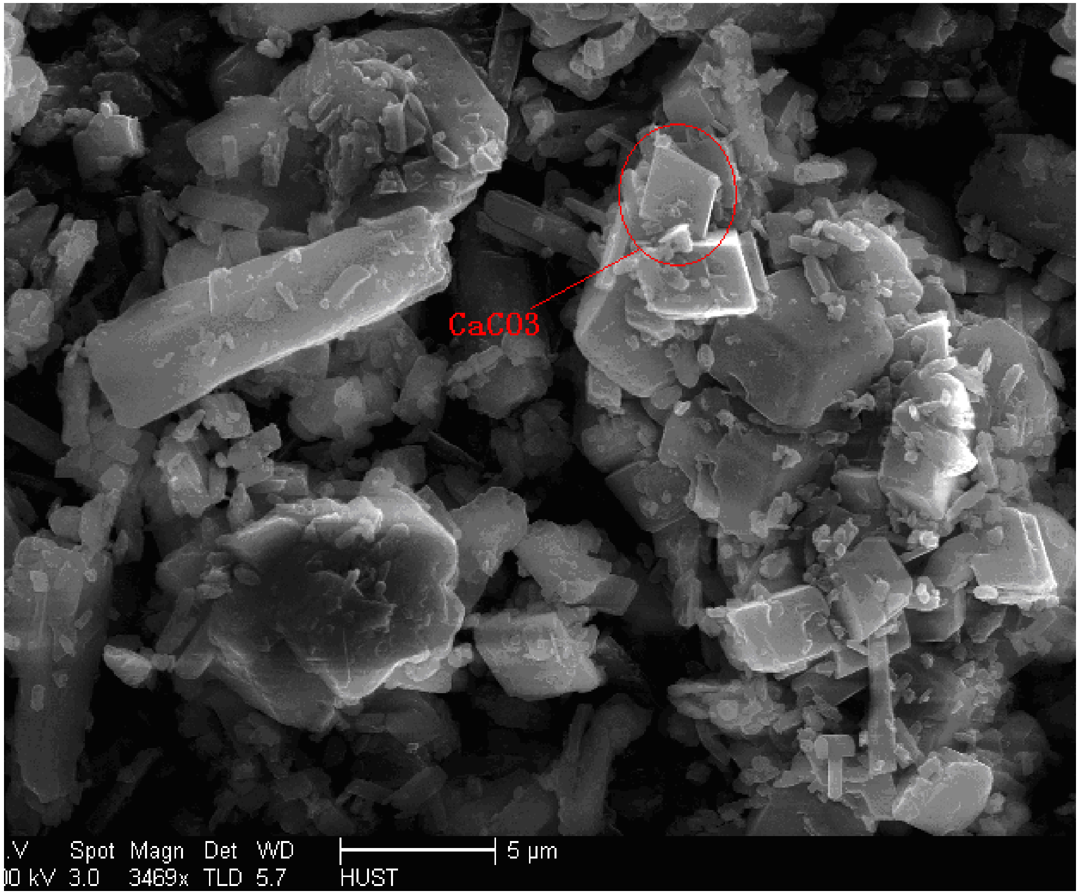
SEM Picture-Wollastonite

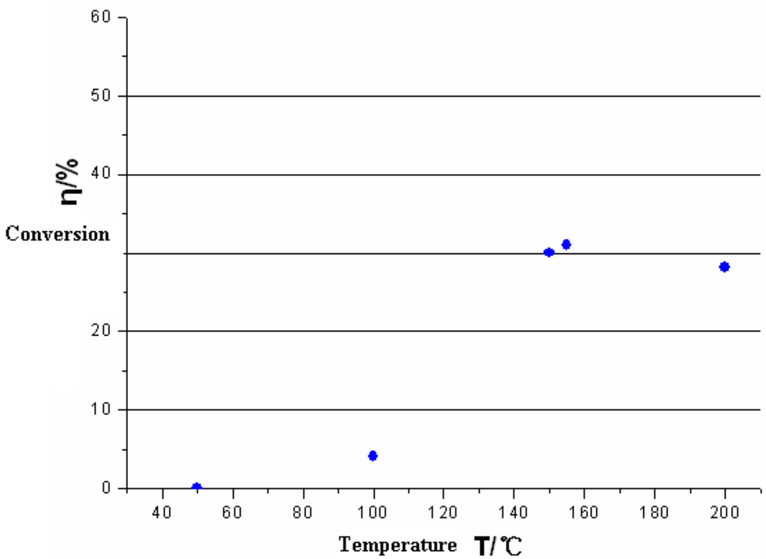


- Wollastonite reaction product. SEM analysis showing the **Calcium carbonate** (**the red loop**) existed in the product.

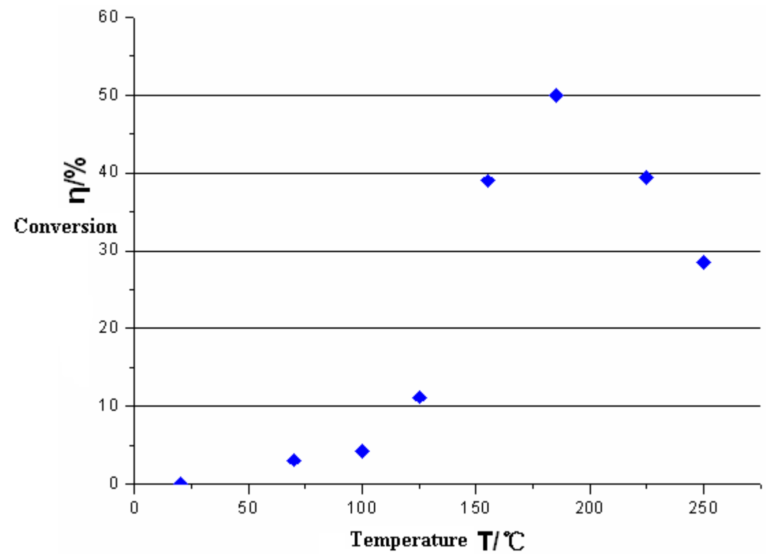
Conversion rate of mineral carbonation

Serpentine			Wollastonite		
Product	Conversion%	Average Conversion%	Product	Conversion%	Average Conversion%
1-1	41.8	42.1	1-1	19.6	17.5
1-2	42.4		1-2	15.5	
2-1	31.7	31.05	2-1	20.5	19.9
2-2	30.4		2-2	19.3	
3-1	57.5	58.05	3-1	41.9	37.7
3-2	58.6		3-2	33.6	
4-1	8.1	8.05	4-1	60.9	57.9
4-2	8.0		4-2	54.9	
5-1	0.1	0.05	5-1	38.8	35.8
5-2	0		5-2	32.8	
6-1	4.1	4.1	6-1	77.2	83.5
6-2	4.1		6-2	89.5	
7-1	30.4	30.05	7-1	57.4	57.2
7-2	29.7		7-2	57.1	
8-1	27.6	28.15	8-1	57.7	60.7
8-2	28.1		8-2	63.8	

Temperature Effect——Serpentine



a. Our Experiment Result



b. Literature Experiment Result

- The results show that the conversion rate of carbonation increases with temperature increasing. As the temperature reaches 150℃, the carbonation conversion rate quickly rise to 30%, after that it decrease little with temperature increasing which maybe related to the decrease of carbon dioxide solubility in high temperature

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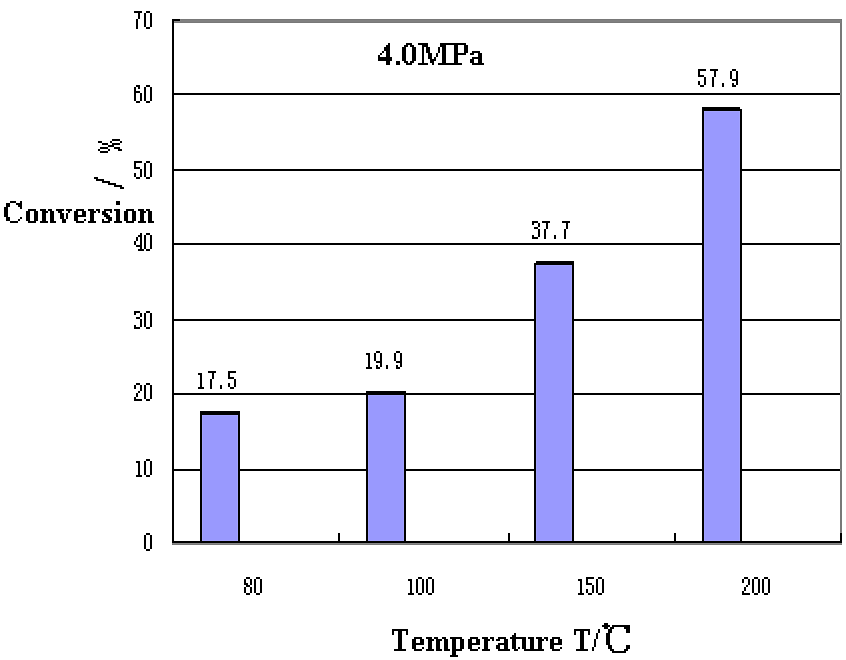
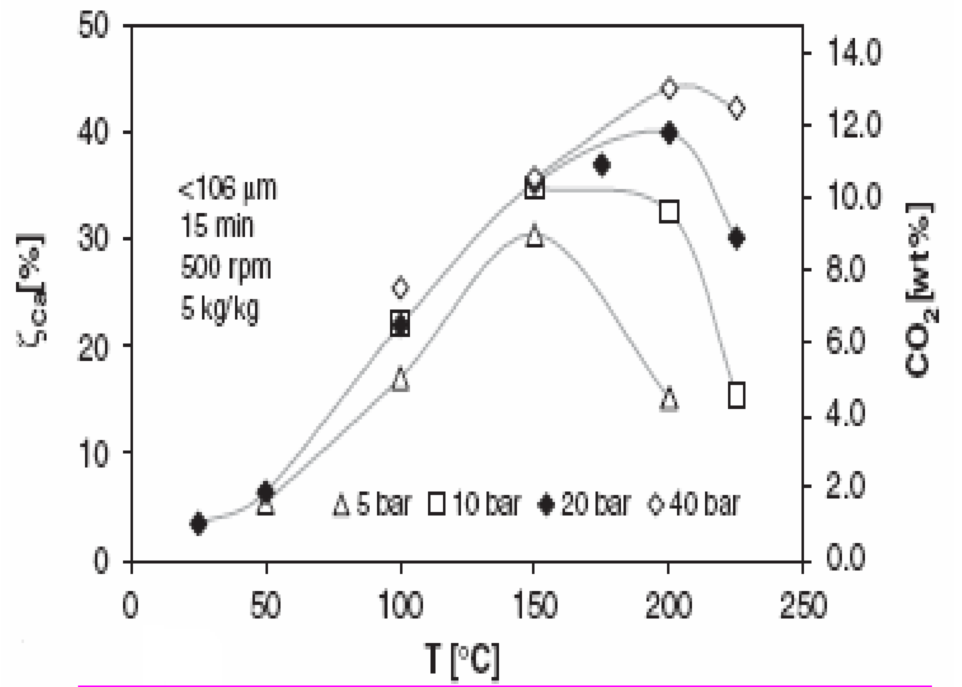
Temperature Effect—Wollastonite



Our Experiment Result



Experiment Result of Wouter J.J. Huijgen

In order to get a high carbonation conversion, we have to choose a suitable temperature to promote the mineral carbonation.

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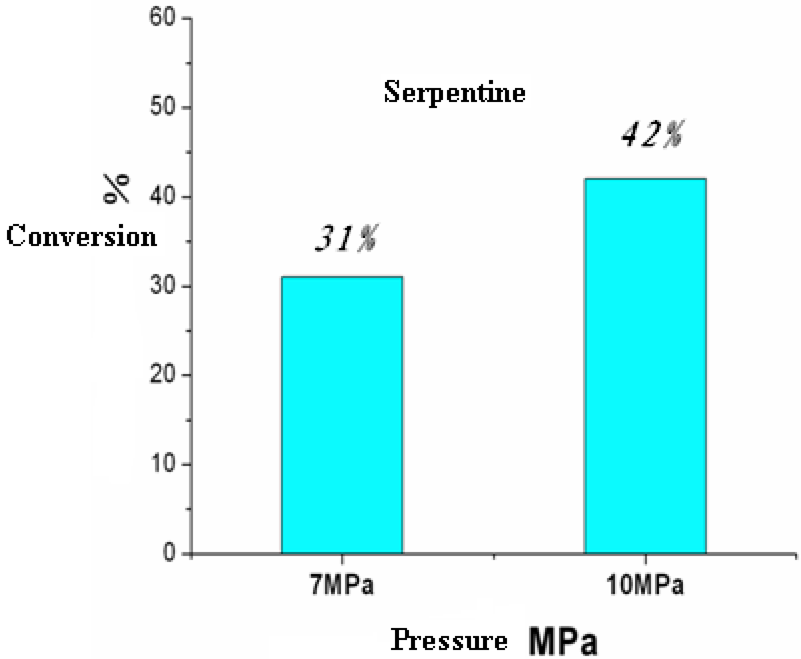
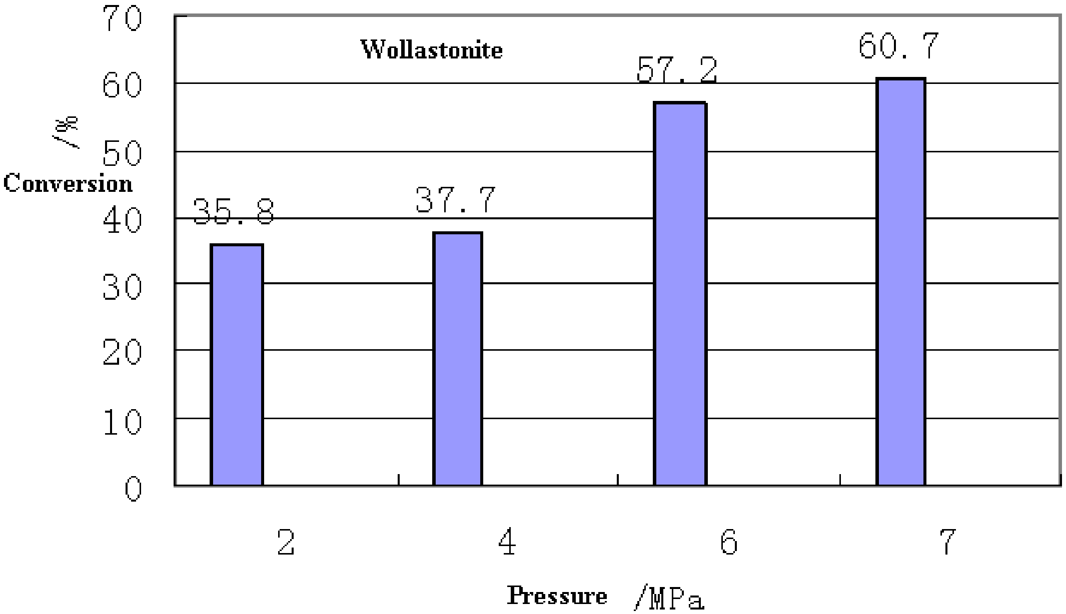
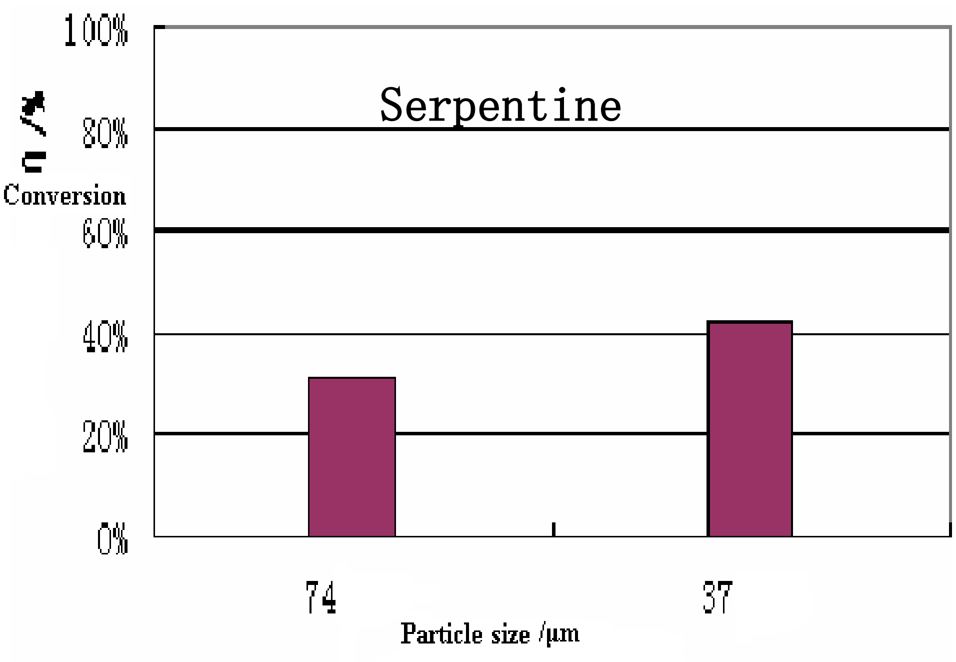
Effect of Pressure

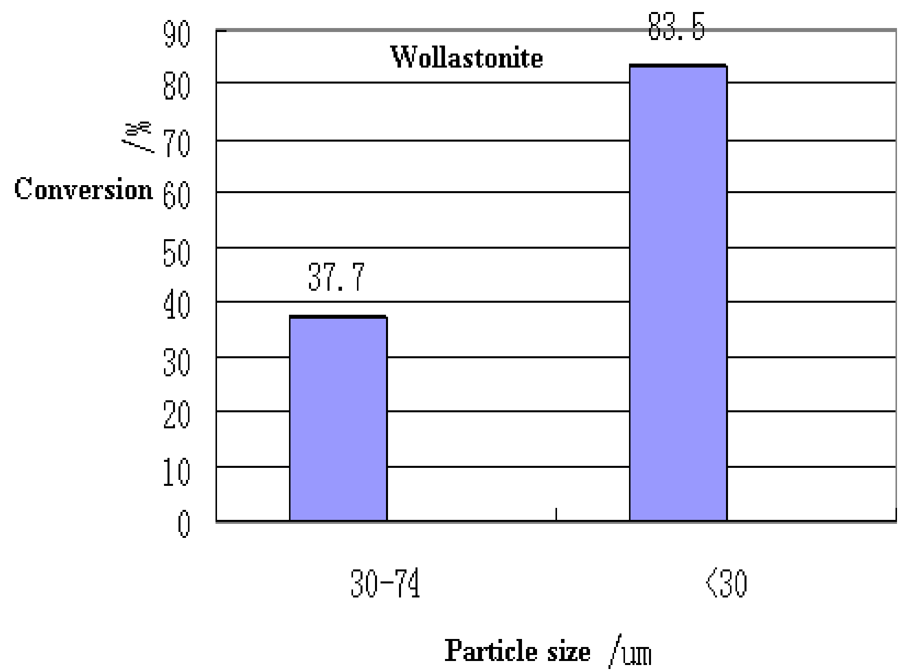




- From the charts we can see that the carbonation conversion rate increases as the pressure increases.
- High pressure can increase of the reaction rate constant. So the conversion rate of the mineral carbonation reaction will increase. But when the pressure increases to above 6MPa, the carbonation conversion rate increases weakly compared to the increase in pressure.

Effect of Particle Size





- Mineral carbonation conversion rate increases with the decrease of the particle size.
- The surface area of the mineral particles increases with particle size decreases.
- In the crushing and screening process, the particle crystal structure was destroyed. This improved the activity of the mineral particles in the reaction.

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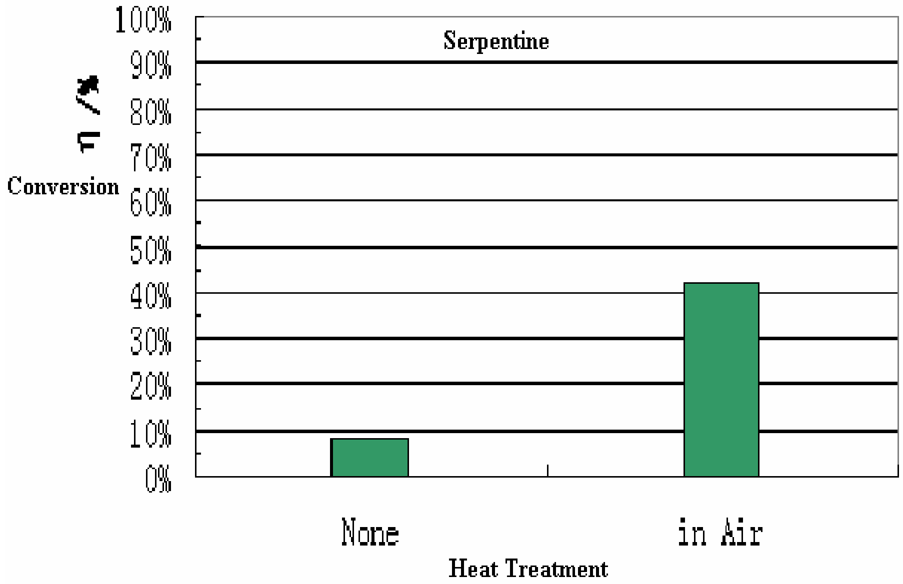
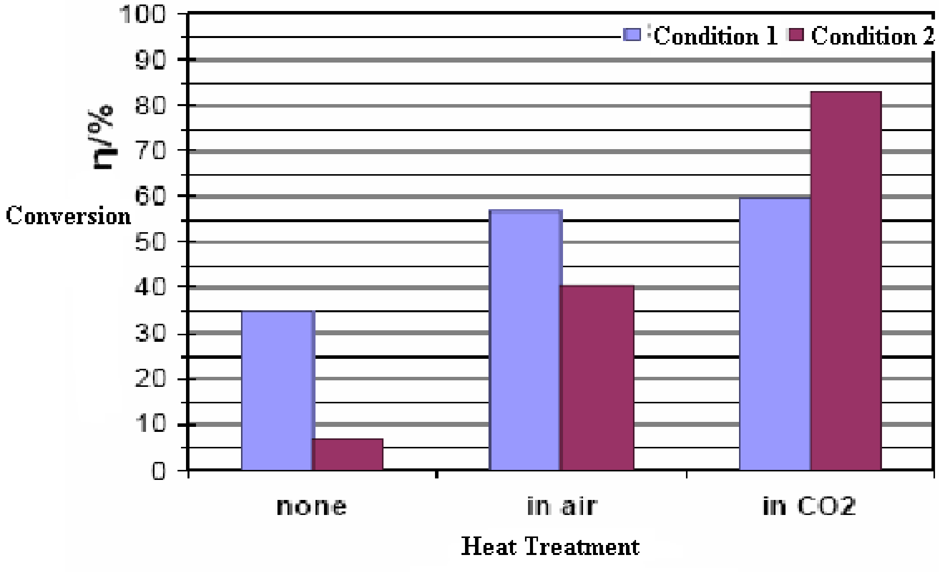
Effect of Heat Treatment



a. Our Experiment Result

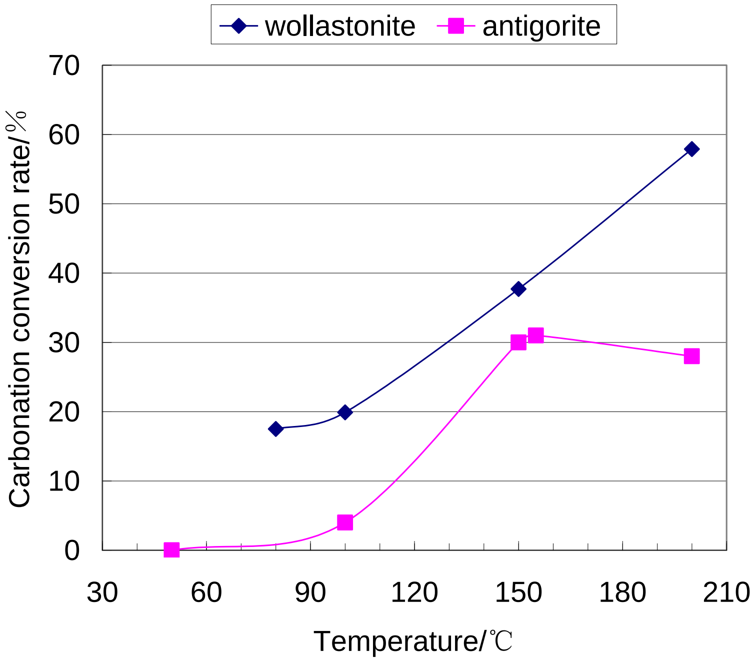


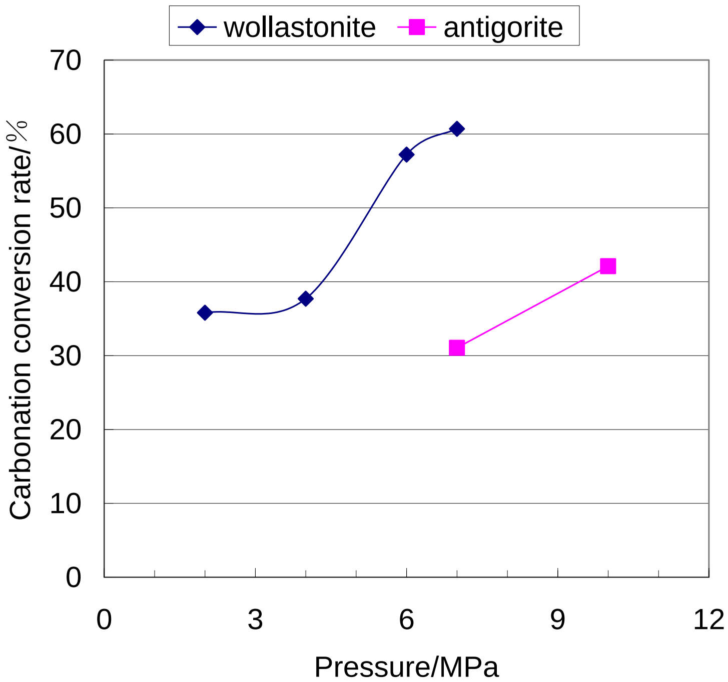
b. Literature Experiment Result

- The impact of heat treatment on the conversion rate is clear. The conversion rate of mineral carbonation after heat treatment is much higher.
- Heat treatment can reduce the water content in the mineral particles, so the quality of the relative percentage of magnesia increases. Thus speeds up the mineral particles dissolved in the solution.

Compare of two different minerals

The effect of temperature





The effect of pressure

- **The conversion rate of wollastonite is higher than Serpentine in different conditions.**

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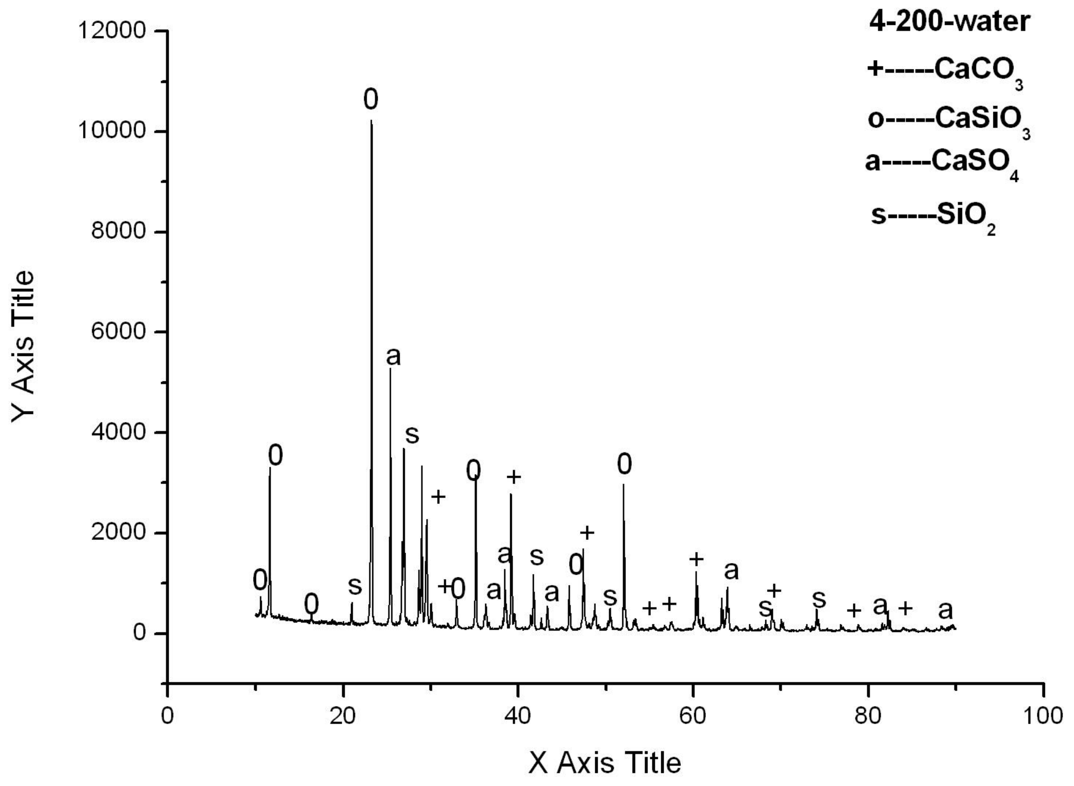
3.3 Mineral Carbonation —— Flue gas

N_2	*81.9%*
O_2	*3%*
CO_2	*15%*
SO_2	*0.1%*

The Reaction Condition

	Experiment condition
1	*P*=6MPa， *T*=150℃， 30~74μm， t=60min
2	*P*=4MPa， *T*=200℃， 30~74μm， t=60min
3	*P*=4MPa， *T*=150℃， 30~74μm， t=60min
4	*P*=4MPa， *T*=100℃， 30~74μm， t=60min
5	*P*=4MPa， *T*=80℃， 30~74μm， t=60min
6	*P*=2MPa， *T*=150℃， 30~74μm， t=60min

carbonation production_ XRD



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Outlet Gas

- $CaSiO_3$------$CaCO_3$
  - Outlet CO_2 : 2.3-5.2 %
  - Outlet SO_2 : 0%
- $MgSiO_3$------$MgCO_3$
  - Outlet CO_2: 2.4-3.4%
  - Outlet SO_2: 0%

- The tests are not finished.

Summary

- The O_2/CO_2 combustion pilot-scale system ;
- Mineral vaporization in the O_2/CO_2 combustion;
- Pure CO2 and flue gas direct mineral carbonation.

Future work

- **PM2.5 in O_2/CO_2 combustion**
- **Trace elements in O_2/CO_2 combustion**
- **CO2 Mineral carbonation of flue gas -- CO2, SO2, NOx, and Hg control**

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THANKS FOR YOUR ATTENTION!